

SCIENCE FOR GLASS PRODUCTION

UDC 666.221.6:666.113.654'621'48'47'16.001.5

FLUOROALUMINATE GLASS
CONTAINING Cd, Zn, AND La FLUORIDESV. D. Khalilev¹ and N. O. Tagil'tseva¹Translated from *Steklo i Keramika*, No. 3, pp. 9 – 11, March, 1998.

In order to obtain glass with an increased index of refraction, oxygen-free fluoroaluminate glass samples containing cadmium, zinc, and lanthanum fluorides were synthesized. Their main physicochemical properties were studied. According to the data from x-ray phase analysis cadmium, zinc, and lanthanum fluorides do not form crystal phase matrices with the components and are present in the form of independent phases. The optical constants of this glass vary within the range of 1.4278 – 1.4303 at an aperture of 0.1.

The fluorine glass category including fluoroaluminate glass is at present the object of intense studies since this glass has a higher softening point (410 – 450°C) and a lower index of refraction at the same level of crystallization stability [1]. The investigations of fluoride glass were mostly carried out on the glass with a refractive index of 1.426. In order to be used in instruments, the glass should have a higher refractive index. The development of fluoroaluminate glass with an increased refractive index is a difficult task since up to 75% of the volume in the structure of this glass is occupied by fluorine atoms, which predetermines its refractometric properties. Therefore, to increase the refractive index the fluorides of cations with high refraction levels should be used, such as lead, cadmium, zinc, and lanthanum. Fluoroaluminate glass containing lead was investigated in [2].

The present paper describes glass containing zinc, cadmium, and lanthanum. The analysis of the published data revealed that glass containing zinc fluorides can be synthesized in $\text{ZnF}_2 - \text{RF}_2$ systems, where R is Ba, Sr, Ca, Cd [3]. Up to now only fluoroaluminosilicate glass containing cadmium and lanthanum fluorides has been developed.

The purpose of our work was to obtain and study fluoroaluminate glass containing zinc, cadmium, and lanthanum fluorides. We expected to identify the variability of the basic physicochemical parameters and structure of the glass depending on introduction of the fluorides listed in the glass composition. In addition, the optical constants of the glass obtained were determined.

The glass was produced in a crucible made of SU-2000 glass carbon in the dried and purified argon at 1000°C for 60 min. The materials used for synthesis were of high purity. In order to avoid crystallization in the course of production of highly crystallizable fluoride glass, the process was performed by two methods:

the vitreous mixture was poured on a massive brass plate and pressed from above with another brass plate. The samples thus obtained were up to 1 mm thick; accelerated cooling.

When employing the second method, a set of two glass carbon crucibles was placed into a special unit consisting of an aluminum radiator and a copper block having an indentation in its central part repeating the imprint of the lower crucible. A lead insert was placed in the hollow of the upper crucible. In such conditions the crucible set with the glass was left until the glass solidified (1.5 min). The glass samples obtained were disk-shaped, 30 mm in diameter and 6 – 7 mm thick. After annealing, these samples were free of stresses.

The vitrification temperature and presence of crystallization in the glass were determined by differential thermal analysis, and the presence and composition of the crystalline phases were determined by x-ray phase analysis of the samples based on the files of the American Scientific Society (1989). Prior to that, forced crystallization of the glass from the melt was carried out with holding at the exothermic effect temperature (520 – 540°C) for 1 hour. The refractive index of the glass was measured with an IRF-23 refractometer. The sample investigated was treated in such a way that its two flat and polished surfaces were placed at an angle of $90^\circ \pm 3^\circ$. The index of refraction was determined for the wave length of 589.3 nm corresponding to the D line of the sodium spectrum and also for lengths of 486.1 and 656.3 nm corresponding to lines F and C of the hydrogen spectrum.

Glass containing 36% AlF_3 and 64% RF_2 , where R is Ba, Sr, Y, Ca, Mg, was selected as the matrix to be modified (here and elsewhere, the molar concentration is indicated). In [4] the principal physicochemical properties and optical constants of this glass were determined: $n_D = 1.426$ and $v_D = 100$. The glass has a wide transparency interval (250 – 6500 nm), which allows it to be considered it as a very convenient vitreous matrix for introduction of the fluo-

¹ St. Petersburg State Technological Institute (Technical University), St. Petersburg, Russia.

rides of *d*- and *f*-elements [5] in which their behavior can be observed over a wide spectral range.

For synthesis of fluoroaluminate glass containing zinc, cadmium, and lanthanum fluorides, the fluorides forming part of the glass were partially replaced with the above listed fluorides, and in addition zinc, cadmium, and lanthanum fluorides were introduced above 100%. The data and the compositions obtained are listed in Tables 1 and 2.

In order to determine the characteristic temperatures of the glass, the derivatograms were obtained. The softening point t_g and the lowest crystallization point t_{cr} of the glass

investigated coincide with t_g and t_{cr} of the matrix being modified and are positioned within the interval of 420–450 and 500–540°C, respectively. The introduction of zinc, cadmium, and lanthanum fluorides does not change the dilatometric curve shape.

Fig. 1 and 2 represent the data from the x-ray phase analysis of the crystallized glass synthesized. As seen from Fig. 1, the crystallization products include, above all, usovite ($\text{Ba}_2\text{CaMgAl}_2\text{F}_{14}$) and a solid solution based on strontium fluoroaluminate (SSSF); in the generalized form, the composition of SSSF is: $(\text{Ca}, \text{Sr}, \text{Ba})\text{AlF}_5$. The crystallization prod-

TABLE 1

Glass*	Content, mole %								Crystalline phases**
	BaF ₂	SrF ₂	CaF ₂	MgF ₂	AlF ₃	YF ₃	CdF ₂	ZnF ₂	
1	12.19	12.19	12.19	12.19	34.29	12.19	4.76	–	SSSF, SSU, CdF ₂ , MgF ₂ , YF ₃
2	11.10	11.10	11.10	12.80	36.00	12.80	5.10	–	SSSF, SSU, MgF ₂ , YF ₃
3	9.60	9.60	9.60	12.80	36.00	12.80	9.60	–	SSSF, CdF ₂ , MgF ₂ , YF ₃
4	12.80	12.80	12.80	10.30	36.00	10.30	5.00	–	SSSF, SSU, CdF ₂ , YF ₃
5	12.80	12.80	12.80	12.80	34.00	12.80	3.00	–	SSSF, SSU, MgF ₂ , YF ₃
6	12.19	12.19	12.19	12.19	34.29	12.19	–	4.76	SSSF, SSU, YF ₃ , ZnF ₂
7	11.10	11.10	11.10	12.80	36.00	12.80	–	5.10	SSSF, SSU, YF ₃ , MgF ₂
8	9.60	9.60	9.60	12.80	36.00	12.80	–	9.60	The same
9	12.80	12.80	12.80	10.30	36.00	10.30	–	5.00	SSSF, SSU, YF ₃ , MgF ₂ , ZnF ₂
10	12.80	12.80	12.80	12.80	34.00	12.80	–	2.00	SSSF, SSU, YF ₃ , MgF ₂
11	13.73	12.55	12.55	12.55	35.29	12.55	–	0.78	SSSF, SSU, YF ₃ , MgF ₂ , ZnF ₂
12	14.23	12.31	12.31	12.31	34.61	12.31	–	1.92	The same
13	12.55	12.55	12.55	12.55	35.29	12.55	0.98	0.98	SSSF, SSU, YF ₃ , MgF ₂ , ZnF ₂ , CdF ₂
14	12.40	12.40	12.40	12.40	36.00	12.40	1.00	1.00	SSSF, SSU, YF ₃ , MgF ₂
15	14.09	12.19	12.19	12.19	34.29	12.19	1.43	1.43	SSSF, SSU, YF ₃ , MgF ₂ , ZnF ₂ , CdF ₂

* Cooling of the melt between two tin plates.

** SSSF) solid solution based on strontium fluoroaluminate SrAlF_5 ; SSU) solid solution based on usovite $\text{Ba}_2\text{CaMgAl}_2\text{F}_{14}$.

TABLE 2

Glass	Content, mol. %									Crystalline phases*
	BaF ₂	SrF ₂	CaF ₂	MgF ₂	AlF ₃	YF ₃	LaF ₃	CdF ₂	ZnF ₂	
1**	12.19	12.19	12.19	12.19	34.29	12.19	4.76	–	–	SSSF, SSU, LaF ₃ , MgF ₂ , YF ₃
2**	11.10	11.10	11.10	12.80	36.00	12.80	5.10	–	–	SSSF, SSU, MgF ₂ , YF ₃
3**	9.60	9.60	9.60	12.80	36.00	12.80	9.60	–	–	SSSF, SSU, LaF ₃ , YF ₃
4**	12.80	12.80	12.80	10.30	36.00	10.30	5.00	–	–	SSSF, SSU, MgF ₂ , YF ₃
5**	12.80	12.80	12.80	12.80	31.00	12.80	5.00	–	–	SSSF, SSU, MgF ₂ , YF ₃
6**	11.80	11.80	11.80	11.80	36.00	11.80	5.00	–	–	SSSF, SSU, LaF ₃ , MgF ₂
7***	12.30	12.30	12.30	12.30	36.00	12.30	2.50	–	–	SSSF, SSU, LaF ₃ , MgF ₂
8***	12.80	10.80	12.80	12.80	36.00	12.80	2.00	–	–	SSSF, SSU, LaF ₃ , MgF ₂ , YF ₃
9**	12.43	12.43	12.43	12.43	34.94	12.43	0.97	0.97	0.97	SSSF, SSU, LaF ₃ , CdF ₂ , ZnF ₂ , YF ₃
10***	12.20	12.20	12.20	12.20	36.00	12.20	1.00	1.00	1.00	SSSF, SSU, LaF ₃ , CdF ₂ , ZnF ₂ , YF ₃
11**	12.08	12.08	12.08	12.08	33.96	12.08	1.88	1.88	1.88	SSSF, SSU, LaF ₃ , CdF ₂ , ZnF ₂ , YF ₃ , MgF ₂
12***	11.60	11.60	11.60	11.60	36.00	11.60	2.00	2.00	2.00	SSSF, SSU, LaF ₃ , CdF ₂ , ZnF ₂ , YF ₃

* SSSF) solid solution based on strontium fluoroaluminate SrAlF_5 , SSU) solid solution based on usovite $\text{Ba}_2\text{CaMgAl}_2\text{F}_{14}$.

** Cooling of the melt between two brass plates.

*** Cooling of the melt in the crucible in the cooling unit.

TABLE 3

Glass, content, mol.%	Optical constants			
	n_C	n_D	n_F	v
Matrix: 36 AlF ₃ , 64 RF ₂ (where R is Ba, Sr, Y, Ca, Mg)	1.4250	1.4265	1.4293	100.0
1.0 ZnF ₂ , 1.0 CdF ₂ , 1.0 LaF ₃ , 36.0 AlF ₃ , 61.0 RF ₂ (where R is Ba, Sr, Y, Ca, Mg)	1.4279	1.4292	1.4322	99.8
2.0 ZnF ₂ , 2.0 CdF ₂ , 2.0 LaF ₃ , 36.0 AlF ₃ , 58.0 RF ₂ (where R is Ba, Sr, Y, Ca, Mg)	1.4294	1.4303	1.4339	95.6
2.5 LaF ₃ , 36.0 AlF ₃ , 61.5 RF ₂ (where R is Ba, Sr, Y, Ca, Mg)	1.4284	1.4278	1.4327	100.0
2.0 LaF ₃ , 10.8 SrF ₂ , 36.0 AlF ₃ , 51.2 RF ₂ (where R is Ba, Y, Ca, Mg)	1.4275	1.4288	1.4318	99.7

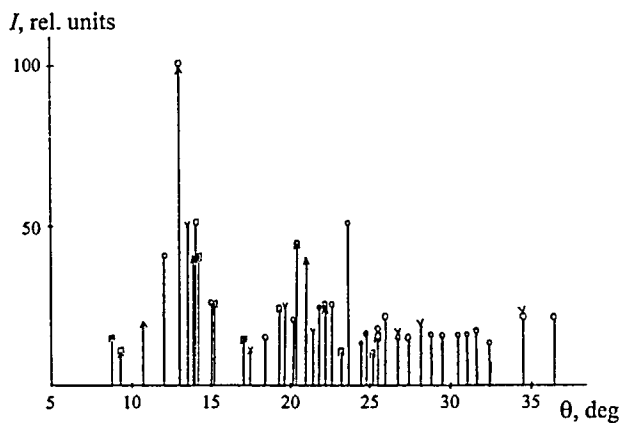


Fig. 1. X-ray diffraction diagram of the crystallized matrix under modification: ^) SSU; \Pi) SSSF; O) YF₃; \vee) MgF₂.

ucts also include yttrium and magnesium fluorides. On introduction of cadmium, zinc, and lanthanum fluorides in the glass composition, they are also detected in the crystallization products (Fig. 2)

Of the series of synthesized glass types, we selected 4 glasses for which the optical constants were determined (Table 3). It is seen that the refractive index of these glasses is higher than that of the matrix under modification.

The efficiency of transmission of light energy from the radiation source through the optical fiber is determined by its numerical aperture

$$N_A = \sqrt{n_1^2 - n_2^2},$$

where n_1 and n_2 are the refractive indexes of the fiber core and the fiber sheath.

The numerical aperture was determined for the 4 glass types selected. The matrix modified was taken as the fiber sheath. The aperture was 0.1 for all 4 types of glass.

Thus, on introduction of zinc, cadmium, and lanthanum fluorides in fluoroaluminate glass, glass samples with the maximum content (%) were obtained: 9.6 ZnF₂, 9.6 CdF₂, 10.0 LaF₃.

The present results can be used for the synthesis of similar glass.

REFERENCES

1. Y. Wang, N. Sawanobori, Sh. Nagahama, "Formation of fluoride glasses based on AlF₃-YF₃-PbF₂ system," *Non-Cryst. Solids*, **128**(3), 322 - 325 (1991).

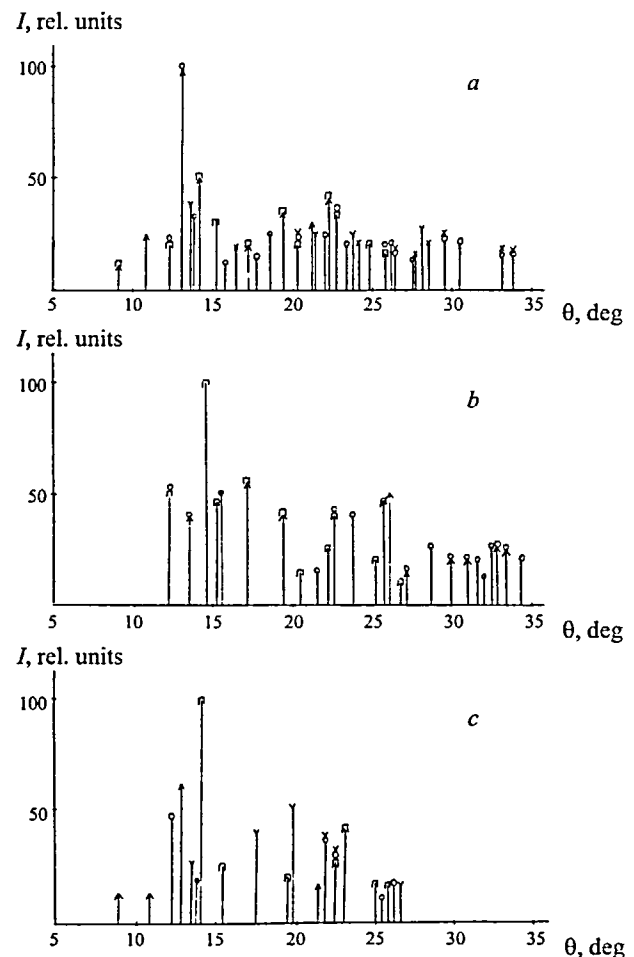


Fig. 2. X-ray diffraction diagrams of crystallized glass containing: a) cadmium fluoride: ^) SSU, \Pi) SSSF, O) YF₃, \vee) MgF₂, \times) CdF₂; b) zinc fluoride: \Pi) SSSF, O) YF₃, ^) ZnF₂; c) lanthanum fluoride: ^) SSU, \Pi) SSSF, \vee) MgF₂, O) LaF₃.

2. M. Kh. Ekzekov, V. G. Chekhovskii, V. V. Ipatov, and V. D. Khalilev, "Crystallization of lead-containing glass and melts based on BaSrCaMgAl₂F₁₄," *Steklo Keram.*, No. 7, 10 - 15 (1992).
3. B. E. Kisman, "Raw materials. Fluoride glasses," *Critical Report on Applied Chemistry*, **27**, Chichester - New York - Brisbane - Toronto - Singapore, 81 - 104 (1989).
4. V. D. Khalilev and V. L. Bogdanov, "Fluoride glasses," *Zh. VKhO im. D. I. Mendeleeva*, **31**(5), 593 - 602 (1991).